Two isomers of a bis(diphenylphosphino)-phosphinine, and the synthesis and reactivity of Ru arene/Cp* phosphinophosphinine complexes†‡

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The reaction of 4,6-di(tert-butyl)-1,3,2-diazaphosphinine (3) with two equivalents of MeCRCPPh$_2$ gave two isomeric products, 2,6-bis(diphenylphosphino)-3,5-dimethylphosphinine (5) and 2,5-bis(diphenylphosphino)-3,6-dimethylphosphinine (6), which were successfully separated and their molecular structures determined by X-ray crystallography. Although the 2,6-bis(iminophosphorano)phosphinine 7 was readily synthesised from 5 using mesityl azide, its coordination to late transition metals was not achieved. The reaction of 2-diphenylphosphino-3-methyl-6-trimethylsilylphosphinine (1) with [{Ru(Cl)(m-Cl)(p-cymene)}$_2$] generated two products: cis-[Ru(Cl)$_2$(1)$_2$] (2) and the dinuclear species [Ru(m-Cl)$_3$(p-cymene)Ru(Cl)(1)] (8), which was characterised by single crystal X-ray diffraction. The reaction of 1 with [{Ru(Cl)(m-Cl)(C$_6$Me$_6$)}$_2$]/NH$_4$PF$_6$ led to cleavage of the SiMe$_3$ group and addition of H$_2$O across a PQC bond to generate [Ru(C$_6$Me$_6$)(1-OH-2-PPh$_2$-3-MePC$_5$H$_4$)][PF$_6$] (9). The reaction of 1 with [{Ru(Cp*)(m$_3$-Cl)}$_4$] yielded [Ru(Cp*)(Cl)(1)] (10) which readily reacted with H$_2$O across a PQC bond to form [Ru(Cp*)(Cl)(1-OH-2-PPh$_2$-3-Me-6-SiMe$_3$PC$_5$H$_3$)] (11). Neither 9, 10, 11 or cis-[Ru(Cl)$_2$(dppm)$_2$] were effective precatalysts for the transfer hydrogenation (TH) of acetophenone, unlike 2 which in addition was also found to catalyse the TH of benzophenone at 82 1C (0.1 mol% 2 with 0.5 mol% KO^{t}Bu in ^{i}PrOH), with much lower activity for 2-fluorobenzaldehyde and 4-methylcyclohexanone. 11 was a competent precatalyst for the hydrogen-borrowing upgrading of EtOH/MeOH to isobutanol, albeit in lower yields compared to 2.

Introduction

Phosphinines (the phosphorus analogue of pyridine) are aromatic heterocycles that are of interest due to their unique properties[1] and for their use as ligands in homogeneous catalysis.[2] Functionalising phosphinines with an additional donor can generate chelating ligands,[3] and much of the recent progress in this area has focused on the development of 2-pyridylphosphinines (the mono-phosphorus analogues of bipyridine).[4] The synthesis of phosphinines with an additional phosphorus donor has also been explored, and chiral ligands containing a phosphine (Chart 1, A)[5] or phosphite donor (B)[6] have been successfully syn-thesised along with phosphinines that contain a phosphinite (C)[7]

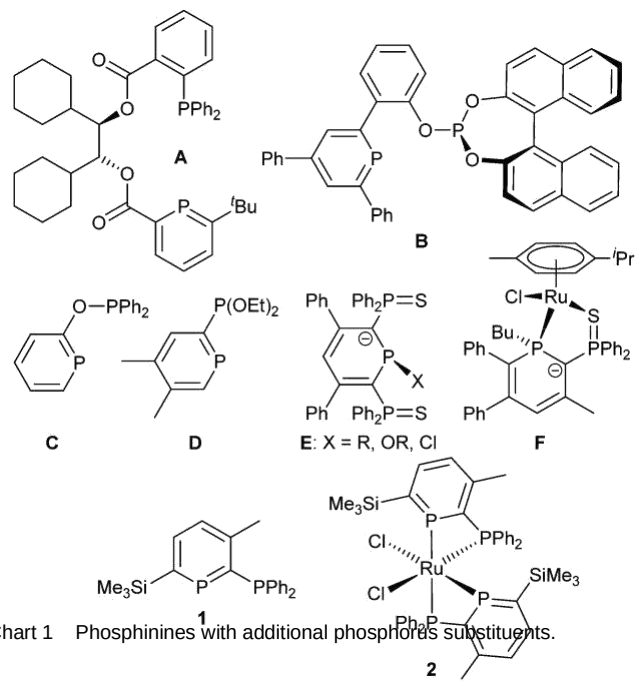

Chart 1 Phosphinines with additional phosphorus substituents.

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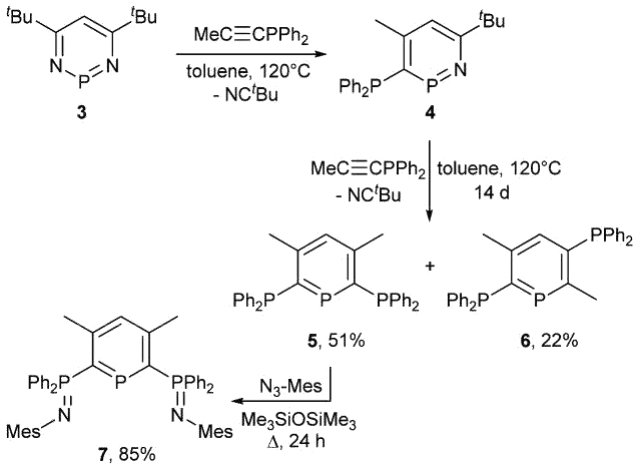
or phosphonite donor (D).[7b,8] Additionally, several diphosphinines,[1d,9] triphosphinines[7a,10] and tetraphosphinine macrocycles[11] are also known.

There are a handful of synthetic methods that give access to 2-phosphinophosphinines,[12] but the diazaphosphinine methodology reported by Mathey and Le Floch represents a simple and versatile route to mono-, di- and tetra-diphenyl-phosphino-substituted phosphinines.[13] 2,6-$(PPh_2)_2$-3,5-Ph_2PC_5H has exclusively been used in reactions with sulfur followed by a nucleophile in order to generate anionic phosphacyclohexadienyl ligands (E),[14] which have shown extensive coordination chemistry,[15] although the aromaticity in the phosphinine ring is lost. We are interested in applying phosphine-substituted phosphinine ligands in homogeneous catalysis, and have previously shown that 2-PPh_2-3-Me-6-$SiMe_3PC_5H_2$ (1) can be used as a chelating ligand to generate cis-$[Ru(Cl)_2(1)_2]$ (2).[16] 2 was an effective precatalyst for the room temperature transfer-hydrogenation of acetophenone derivatives and the H-borrowing upgrading of EtOH/MeOH to isobutanol.[16] Prior to this study, 2-phosphinophosphinine ligands were only characterised as bridging ligands.[8,17] Further examples of 1 as a small-bite angle[18] chelating ligand were subsequently described in a series of group 6 tetracarbonyl complexes, with 1 also able to influence the selectivity of Cr-catalysed ethylene oligomerisation reactions,[19] as well as in the Rh-catalysed hydroboration of carbonyls.[20] We now describe the extension of the synthetic route used to synthesise 1 to give bis(diphenylphosphino)phosphinines. In addition, the coordination chemistry of phosphinophosphinines using addi-tional Ru starting materials was explored because this area is still very limited; the only structurally characterised Ru phosphinine complexes are trans-$[Ru(Cl)_2(PC_5H_5)_4]$,[21] $[Ru(Cp^*)(2,6\text{-}(SiMe_3)_2\text{-}PC_5H_3)][BF_4]$[22] and Ru complexes containing 2,2′-biphosphinines.[23] F, containing a 2-(phosphinesulfide)phosphacyclohexadienyl ligand, has also been characterised.[13c]

Results and discussion

Bis(phosphino)phosphinines

As was observed in the synthesis of 1,[16] the reaction of one equivalent of $MeCRCPPh_2$ with the diazaphosphinine 3[13] regioselectively formed one azaphosphinine isomer containing an ortho-phosphine substituent within two hours in toluene at 120 1C in a sealed vessel (Scheme 1, 4). However, reaction with a second equivalent of $MeCRCPPh_2$ proceeded considerably more slowly, requiring two weeks at 120 1C for complete con-sumption of the azaphosphinine. $^{31}P\{^1H\}$ NMR spectroscopy revealed that two isomeric phosphinines, 5 and 6, were produced in an approximately 60 : 40 ratio respectively (Scheme 1), unlike the analogous reaction for $PhCRCPPh_2$ which was reported to cleanly generate the 2,6-isomer after 20 h at 120 1C.[13a,13b] Separation of the two regioisomers was readily achieved without the need for chromatographic purification due to their different solubilities. 5 is relatively soluble in aliphatic solvents, and was extracted using petroleum ether at 20 1C. After recrystallisation from toluene at 25 1C, analytically pure 5 was obtained in



Scheme 1 Synthesis of bis(phosphino)phosphinines and a bis(imino-phosphorano)phosphinine.

51% yield as a colourless powder that is air-stable in the solid state but decomposes under air within hours in solution. $^{31}P\{^1H\}$ NMR spectroscopy was used to identify the 2,6-isomer, with a triplet resonance at d = 244.8 ppm for the phosphinine P atom and a doublet resonance of greater intensity at d = 8.1 ppm for the equivalent PPh_2 groups. Purification of the 2,5-isomer was achieved by Soxhlet extraction of the remaining residue from the diazaphosphinine reaction using n-hexane heated under reflux over seven days. The 2,5-isomer is more stable to atmo-spheric air and moisture than the 2,6 isomer and the extraction was successfully carried out under air. Recrystallisation from toluene at 25 1C yielded 6 as a colourless solid in moderate yield (22%). $^{31}P\{^1H\}$ NMR spectroscopy demonstrated the inequivalence of the two PPh_2 groups as two resonances at low chemical shift; a doublet-of-doublets at d = 9.1 ppm and another at d = 10.4 ppm with much smaller coupling constants. The phosphinine P atom was also observed at d = 220.8 ppm as a doublet-of-doublets. Single crystals of the 2,6-isomer suitable for X-ray diffraction were grown from a mixture of THF and pet. ether at 25 1C, and the 2,5-isomer from a THF solution layered with Et_2O. The solid-state structure of 5 shows a C_2-symmetric structure with one Ph group in each PPh_2 unit pointing towards the open space around the phosphinine P atom, with the other two orientated anti to each other (Fig. 1, left). Analysis of the ring bond lengths and angles confirmed that the ring is symmetric and is in agreement with the aromatic nature of the phosphinine ring (Table 1). The P(1)–C(1)/P(1)–C(5) bond lengths are slightly contracted with respect to the P(1)–C(1) bond length of 1 (1.741(1) versus 1.754(3) Å for 1).[16] The solid-state structure of the 2,5-isomer showed disorder in the central phosphinine ring (P1 and C1–C7), which was successfully modelled over two positions. Although the location of the PPh_2 groups in the 2,5-positions was established (Fig. 1, right), the disorder makes discussion of the bond lengths and angles unwarranted.

The derivatisation of the 2,6-isomer into its bis(iminophos-phorano)phosphinine analogue was successfully achieved by the Staudinger reaction using mesityl azide in 85% yield (Scheme 1). 7 is structurally related to the well-known bis(imino)pyridine

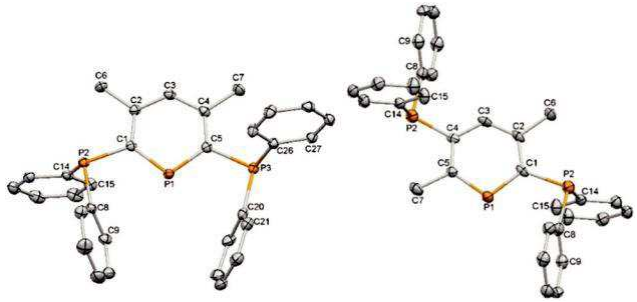


Fig. 1 Molecular structure of 5 (left) and 6 (right; thermal ellipsoids at 50%). All H-atoms and the 2nd positions of the phosphinine ring in 6 have been removed for clarity.

Table 1 Selected bond lengths and angles for 5

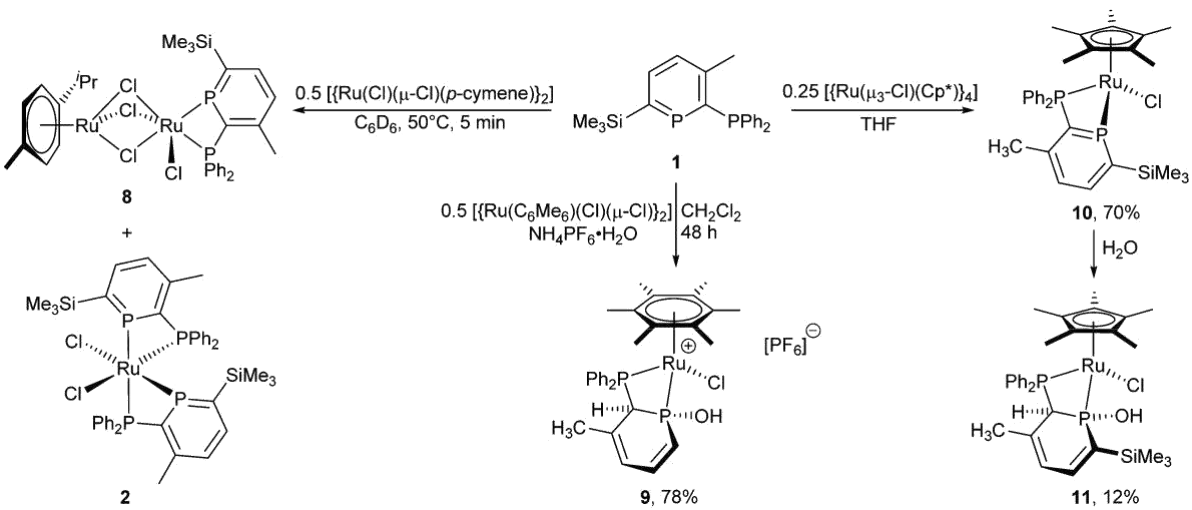
Bond lengths (Å)		Bond angles (1)	
P(1)–C(1)	1.741(1)	P(1)–C(1)–C(2)	124.01(9)
C(1)–C(2)	1.409(1)	C(1)–C(2)–C(3)	121.5(1)
C(2)–C(3)	1.394(2)	C(2)–C(3)–C(4)	126.1(1)
C(3)–C(4)	1.399(2)	C(3)–C(4)–C(5)	121.8(1)
C(4)–C(5)	1.406(2)	C(4)–C(5)–P(1)	123.73(9)
C(5)–P(1)	1.742(1)	C(5)–P(1)–C(1)	102.76(5)
C(1)–P(2)	1.836(1)	P(1)–C(1)–P(2)	118.52(6)

ligands that have been extensively applied in homogeneous catalysis,[24] although the ligand properties are very different as it incorporates two 'hard' iminophosphorane donors[25] along with a 'soft', p-accepting central phosphinine donor (using the HSAB classification). 7 is very moisture-sensitive and must be handled using rigorously dried solvents and under careful exclu-sion of air. Unfortunately, single crystals suitable for X-ray diffraction could not be obtained, but ^{1}H, ^{13}C and ^{31}P{^{1}H} NMR spectroscopic data, as well as HRMS and elemental analysis, were in agreement with the proposed structure. The phosphinine P resonance was clearly observed at d = 246.9 ppm as a triplet ($^{2}J_{P–P}$ = 99.7 Hz) and the two iminophosphorane P atoms were observed as a doublet at d = 9.4 ppm. The mesityl Me groups were observed as two singlets in a 12 : 6 ratio by ^{1}H NMR spectroscopy, and the Me substituents on the phos-phinine ring appeared as a singlet in the same region. Many of the aryl-H signals appeared as overlapping multiplets, but the 4-H atom on the phosphinine ring was observed as a singlet at d = 6.71 ppm.

Many reactions aimed at exploring the coordination chem-istry of 7 with late transition metals were attempted without success. No reaction was observed with [Rh(Cl)(PPh$_3$)$_3$] and [{Rh(m-Cl)(COD)}$_2$], and multiple products were observed in reactions with [Pt(Cl)$_2$(COD)], [{Rh(m-Cl)(CO)$_2$}$_2$] and cis-[Ru(Cl)$_2$(dmso)$_4$] which could not be characterised further. Ultimately, simple coordination of 7 has not yet been achieved with these metals, with the formation of multiple products and loss of aromaticity in the phosphinine ring observed instead. The reaction with FeCl$_2$ gave similar results, as indicated by ^{31}P{^{1}H} NMR spectro-scopy, however, single crystals of one of the products were grown from the reaction mixture. X-ray diffraction confirmed the basic framework of ligand 7, but also highlighted additional reactivity of this ligand with protonation of both PQN bonds and functionalisation of the phosphinine P atom with both O and H (7Fe, see ESI‡). The reason for this lack of success is not known, but the unusual combination of two types of polar-opposite donors (a soft, p-accepting phosphinine with two hard, s-donating iminophosphoranes) could result in a ''mismatched'' ligand with little propensity to coordinate to late transition metals. However, the coordination chemistry with other 'harder' Lewis acids may prove more fruitful because Zn and Mg complexes with neutral iminophosphorane ligands based on dibenzofuran scaffolds are well known.[26]

Ru coordination chemistry

The coordination of 1 to Ru was readily achieved by the reaction of 1 with cis-[Ru(Cl)$_2$(dmso)$_4$],[16] so reactions using this Ru pre-cursor with the two bis(phosphino)phosphinines were attempted. The reaction of two equivalents of 5 or 6 with cis-[Ru(Cl)$_2$(dmso)$_4$] was anticipated to yield the bis-chelating complex that would



Scheme 2 Synthesis of Ru phosphinophosphinine complexes.

feature uncoordinated PPh_2 donors with great potential for further reactivity and coordination chemistry. Unfortunately, reactions with both of the isomers generated multiple products, as observed by $^{31}P\{^1H\}$ NMR spectroscopy, and clean conversion to a single product was not achieved. Purification by crystalli-sation was also unsuccessful, so our efforts instead focused on extending the coordination chemistry of 1 with additional Ru complexes (Scheme 2). The reaction of 1 with 0.5 equivalents of the para-cymene dimer $[\{Ru(Cl)(m\text{-}Cl)(p\text{-cymene})\}_2]$ at 50 1C for 5 min was carried out and the reaction was analysed by $^{31}P\{^1H\}$ NMR spectroscopy. It was observed that all of the proligand 1 had been consumed and that two products had been formed in an approximately 1 : 1 ratio, with the characteristic signals of 2 allowing it to be readily assigned as one of these products.[16] Initially, it was expected that the second product (d = 231.4 (d) and 21.7 (d) ppm) would be mononuclear and possess a half-sandwich geometry (cf. 9), but analysis by single crystal X-ray diffraction of the dark red crystals formed from layering the reaction mixture with pet. ether showed a dinuclear compound 8 (Fig. 2). The structure that was obtained was the result of displacement of one p-cymene ligand instead of separation of the dimer by breaking the two dative Cl - Ru bonds.[27] Ru1 is in a distorted octahedral geometry with one chelating diphos-phinophosphinine ligand and four bonds to Cl atoms, one of which is a terminal ligand. Ru2 has an Z^6-cymene ligand and bonds to three bridging Cl ligands. The bond lengths and angles for the phosphinophosphinine ligand are similar to that previously described in complex 2 with the Ru–phosphinine bond distance shorter than the Ru–PPh_2 distance (Table 2). The P(1)–C(5)–P(2) angle is more acute than in 2 (93.1(1)1 versus 97.7(3)1 in 2), although the P(1)–Ru(1)–P(2) bite-angle has not changed significantly. Unfortunately, insufficient material could be separated from samples of 8, due to co-crystallised 2, to allow for complete characterisation. Attempts were made to optimise the reaction conditions to favour the exclusive formation of 8, however, varying the equivalents of 1 (including a 1 : 1 reaction)

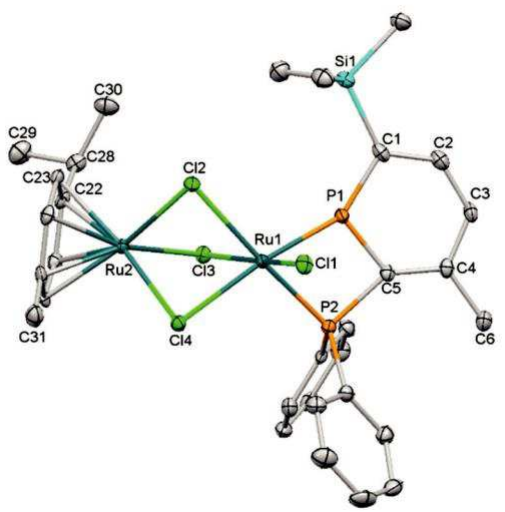


Fig. 2 Molecular structure of 8 with thermal ellipsoids at 50% probability. All H-atoms removed for clarity.

Table 2 Selected bond lengths and angles for the Ru phosphinophos-phinine complexes. Values for only one molecule in the asymmetric unit are given due to the similar values observed for the other molecule

Compound	Bond lengths (Å)		Bond angles (1)	
8	P(1)–C(1)	1.713(3)	P(1)–C(1)–C(2)	114.9(2)
	C(1)–C(2)	1.409(4)	C(1)–C(2)–C(3)	128.9(3)
	C(2)–C(3)	1.397(4)	C(2)–C(3)–C(4)	125.2(3)
	C(3)–C(4)	1.405(4)	C(3)–C(4)–C(5)	117.8(3)
	C(4)–C(5)	1.396(4)	C(4)–C(5)–P(1)	125.1(3)
	C(5)–P(1)	1.717(3)	C(5)–P(1)–C(1)	108.2(1)
	C(5)–P(2)	1.837(3)	P(1)–C(5)–P(2)	93.1(1)
	P(1)–Ru(1)	2.184(1)	P(1)–Ru(1)–P(2)	70.56(3)
	P(2)–Ru(1)	2.283(1)	Cl(1)–Ru(1)–Cl(3)	169.60(2)
	Ru(1)–Cl(1)	2.395(1)		
	Ru(1)–Cl(2)	2.495(1)		
	Ru(1)–Cl(3)	2.428(1)		
	Ru(1)–Cl(4)	2.484(1)		
	Ru(2)–Cl(2)	2.422(1)		
	Ru(2)–Cl(3)	2.458(1)		
	Ru(2)–Cl(4)	2.447(1)		
9	P(1)–C(1)	1.861(3)	P(1)–C(1)–C(2)	118.9(2)
	C(1)–C(2)	1.505(4)	C(1)–C(2)–C(3)	121.4(3)
	C(2)–C(3)	1.328(6)	C(2)–C(3)–C(4)	126.2(4)
	C(3)–C(4)	1.453(6)	C(3)–C(4)–C(5)	126.5(4)
	C(4)–C(5)	1.338(5)	C(4)–C(5)–P(1)	121.8(3)
	C(5)–P(1)	1.774(3)	C(5)–P(1)–C(1)	102.5(2)
	C(1)–P(2)	1.880(3)	P(1)–C(1)–P(2)	92.2(1)
	P(1)–O(1)	1.667(3)	P(1)–Ru(1)–P(2)	71.53(3)
	P(1)–Ru(1)	2.286(1)		
	P(2)–Ru(1)	2.326(1)		
	Ru(1)–Cl(1)	2.401(1)		
11	P(1)–C(1)	1.860(4)	P(1)–C(1)–C(2)	118.5(3)
	C(1)–C(2)	1.504(5)	C(1)–C(2)–C(3)	121.9(4)
	C(2)–C(3)	1.346(6)	C(2)–C(3)–C(4)	126.2(4)
	C(3)–C(4)	1.463(6)	C(3)–C(4)–C(5)	127.8(4)
	C(4)–C(5)	1.358(6)	C(4)-C(5)-P(1)	118.6(3)
	C(5)–P(1)	1.783(4)	C(5)–P(1)–C(1)	105.7(2)
	C(1)–P(2)	1.884(4)	P(1)–C(1)–P(2)	91.1(2)
	P(1)–O(1)	1.628(3)	P(1)–Ru(1)–P(2)	71.84(3)
	P(1)–Ru(1)	2.280(1)		
	P(2)–Ru(1)	2.276(1)		
	Ru(1)–Cl(1)	2.450(1)		

and the reaction temperature did not result in anything other than a mixture of two products. A 4 : 1 reaction of 1:$[\{Ru(Cl)(m\text{-}Cl)\text{-}(p\text{-cymene})\}_2]$ resulted in the selective formation of 2, and 8 could represent an intermediate in this synthetic pathway.

In order to circumvent the issue of the lability of the p-cymene ligand, the reaction was repeated with the hexa-methylbenzene dimer $[\{Ru(Cl)(m\text{-}Cl)(C_6Me_6)\}_2]$ using strictly anhydrous salts of non-coordinating anions to exchange the Cl counteranion that would be formed upon chelation of 1 (Scheme 2). $AgBF_4$, $AgSbF_6$ and $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ generated multiple products, however, NH_4PF_6 cleanly produced a single product by $^{31}P\{^1H\}$ NMR spectroscopy, although the observed chemical shifts (d = 11.6 (d) and 8.8 (d) ppm) indicated that the phosphinine ligand was no longer aromatic. NH_4PF_6 is hygro-scopic, but attempts to repeat the reaction with dried NH_4PF_6 led to multiple products indicating an important role for the adsorbed water in selectively yielding one product. Additionally, without NH_4PF_6, displacement of C_6Me_6 occurs and complex 2 is formed (see ESI‡). Single crystals of the product were grown by slow diffusion of petroleum ether into a CH_2Cl_2 solution of

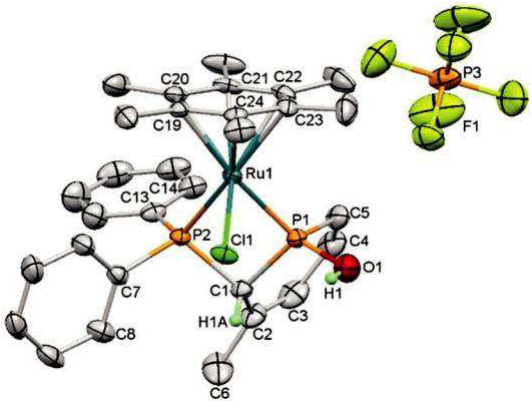


Fig. 3 Molecular structure of 9 with thermal ellipsoids at 50% probability. All H-atoms except those resulting from the reaction with H_2O removed for clarity along with the other cation and anion in the asymmetric unit.

the product in good yield (78%), and the resulting orange needles were analysed by X-ray diffraction, revealing 9 to be the product of the syn-reaction of the phosphinine with H_2O, and the unexpected cleavage of the $SiMe_3$ group (Fig. 3). The Ru atom is bonded to Cl, an Z^6-C_6Me_6 and a chelating phospha-cyclohexadiene ligand which has formed from the addition of H_2O across a PQC double bond. As ammonium salts are hygro-scopic, it is likely that the NH_4PF_6 was the source of the water. It was also observed that the trimethylsilyl substituent had been cleaved, possibly through reaction with F arising from disso-ciation from the PF_6 anion. Cleavage of $SiMe_3$ using HCl has been observed previously.[19,28]

The molecular structure of 9 shows P(1) in a distorted tetrahedral geometry, resulting from sp^3 hybridisation. As expected, the loss of aromaticity in the phosphacyclohexadiene ligand has had a notable effect on the bond lengths and angles around the ring. The C(1)–C(2) bond has lengthened signifi-cantly (1.505(4) Å) in line with a bond order of one, whilst the C(2)–C(3) and C(4)–C(5) bonds (1.328(6) and 1.338(5) Å respec-tively) are shorter than in 1 (1.404(4) and 1.396(4) Å respectively) due to localisation of the CQC double bonds. Both P(1)–C(1) and P(1)–C(5) bonds have lengthened (1.861(3) and 1.774(3) Å respectively) compared to 1 (1.754(3) and 1.749(3) Å respectively in 1). The reaction of coordinated phosphinine ligands with water is well precedented.[1d,7a,29] Pyridylphosphinine ligands coordinated to Pd, Pt,[29] Rh and Ir[30] readily react with water or alcohols across a localised PQC double bond, with Pd/Pt complexes demonstrating syn-addition[31] but anti-addition for Ir and Rh.[30] We have explored the chemistry of BH_3-protected phosphinophosphinine ligands,[16,19] and BH_3 protection of the PPh_2 does not increase the reactivity of the phosphinine unit. BH_3 does not coordinate to the phosphinine, and hence does not lead to enhanced reactivity of the phosphinine with H_2O, because phosphinines are not basic (pK_a E 16)[2b] and so protonation is also not a feature of their chemistry as it is for phosphines.

In order to prepare a half-sandwich complex with an aro-matic phosphinine ligand, 1 was reacted with 0.25 equivalents of [{Ru(Cp*)(m_3-Cl)}$_4$] (Scheme 2). The reaction proceeded

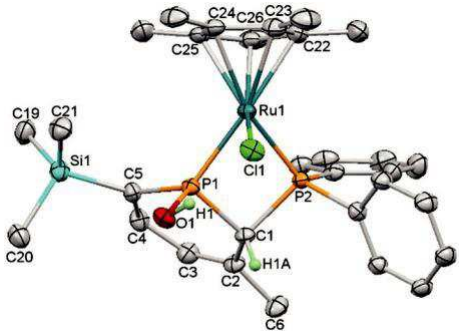


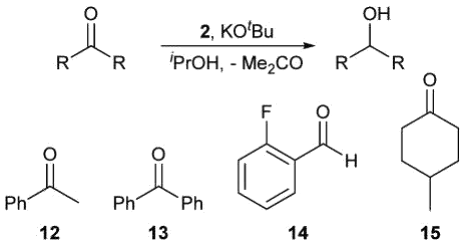
Fig. 4 Molecular structure of 11 with thermal ellipsoids at 50% probability. Only one molecule present in the asymmetric unit is shown and all of the H atoms except those resulting from reaction with H_2O removed for clarity.

rapidly in THF, with a colour change to deep red observed within seconds. The resulting complex proved to be very soluble, however, upon storing a concentrated pet. ether solution at 0 1C, the product precipitated and was collected as an orange solid in 70% yield. $^{31}P\{^1H\}$ NMR showed two doublets at d = 240.1 and 18.2 ppm, and the ^1H NMR spectroscopic data was also in-line with the anticipated half-sandwich compound. The 4-H phos-phinine resonance was observed at d = 6.46 ppm as an apparent doublet-of-triplets due to two similar $^4J_{H-P}$ couplings, and the 5-H resonance at d = 7.63 ppm as a doublet-of-doublets. HRMS confirmed the anticipated formula, but the compound readily reacted with trace moisture which precluded successful elemental analysis. This was definitively established when the compound was exposed to atmospheric moisture and then crystallised from petroleum ether at 5 1C. Single crystal X-ray diffraction proved that, similarly to the synthesis of 9, 10 had reacted with water in a syn-manner, although the trimethylsilyl group had not been cleaved (Fig. 4). Analogous reactivity with isoelectronic [M(Cp*)(pyridylphosphinine)][Cl] (M = Rh, Ir) complexes has previously been established,[30] and subsequent work demonstrated the catalytic potential of a cyclometalated phosphinine iridium(III) complex for water oxidation.[3d] A Pd complex of 2-diphenylphosphinito-phosphinine also recently showed facile hydrolysis in a similar manner to 10.[7a] 11 was obtained in 12% yield ($^{31}P\{^1H\}$ d = 78.3 (d), 18.0 (d) ppm). As with 9, the structure of 11 shows that P(1) has a distorted tetra-hedral geometry, with the H and OH groups in a syn orientation. The bond lengths and angles in 11 are very similar to 9 due to their similar structures. There are few substantial differences in the bond lengths, although the P(2)–Ru(1) bond length (Ru–PPh_2) has decreased slightly (2.276(1) Å in 11 compared to 2.326(1) Å in 9). This was unexpected considering that the P(1)–Ru(1) bond lengths (2.280(1) Å compared to 2.286(1) Å for 9) are nearly identical despite the different electronics of the phosphacyclohexadienyl ligand due to the lack of a $SiMe_3$ substituent in 9.

Transfer hydrogenation and hydrogen-borrowing catalysis

Octahedral Ru bis(phosphinophosphinine) complex 2 displayed high activity in the room temperature transfer hydrogenation of acetophenones (12) at 0.1 mol% loading with 0.5 mol% KO^{t}Bu

Table 3 Transfer hydrogenation of ketones



Substrate	2 (mol%)	Temp. (1C)	Time (h)	Yield[a] (%)	Ref.
12	0.1	20	1	94	16
13	0.1	20	24	70	
	0.1	82	4	95	
14	0.1	20	24	0	
	0.1	82	96	6	
	1	82	24	24	
15	1	82	1	63	

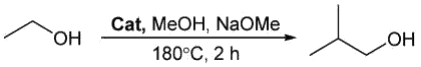
Conditions: 2, KO^{t}Bu (0.5 mol%), ^{i}PrOH (0.4 M [substrate]).[a] Conver-sion determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxy-benzene as an internal standard.

after 1 hour.[16] In an extension to this initial study, several other common substrates were tested (Table 3): benzophenone (13) as an example of a diaryl ketone, an aldehyde (14) and a dialkyl ketone (15). Whilst good conversions were achieved for several acetophenones using 0.1 mol% 2 within one hour,[16] decreased reactivity was observed for 13–15. The room temperature transfer hydrogenation of benzophenone required 24 h to reach the maximum yield (70%), but this could be increased to 95% upon heating to 82 1C for four hours. 2-Fluorobenzaldehyde was tested as a representative aldehyde because electron-poor acetophenones were previously found to be better substrates,[16] but no conversion was observed at room temperature. An increase in catalyst loading (1 mol%), reaction time (24 h) and temperature (82 1C) still only gave low yields of the alcohol (24%). For 4-methylcyclohexanone, using 1 mol% 2 at 82 1C, a 63% yield of 4-methylcyclohexanol was observed within one hour. There is evidence that cyclohexanone can be a more challenging substrate than acetophenone,[32] but the excellent activities observed for 2 at room temperature appear to be limited to aryl-substituted ketones.

The catalytic activity of 9, 10 and 11 was then evaluated using acetophenone under the same conditions as reported for 2,[16] but no activity was found for these three complexes. Either the presence of an arene or Cp* co-ligand does not produce an active catalyst, or a phosphacyclohexdiene ligand, resulting from the addition of H_2O, is not conducive for catalysis. As limited examples of transfer hydrogenation catalysts with P-donor ligands have been reported in the literature,§ [33] cis-[Ru(Cl)$_2$(dppm)$_2$] (dppm = bis(diphenylphosphino)methane) was investigated as a precatalyst in order to probe whether or not the activity of 2 was due to the narrow bite-angle of

§ cis-[Ru(Cl)$_2$(PPh$_3$)$_3$] is a known precatalyst for the transfer hydrogenation of ketones, however, it is not as active as 2, only achieving a 75% yield with aceto-phenone as the substrate after six hours at 82 1C.[48]

Table 4 Catalytic upgrading of ethanol and methanol to isobutanol



Catalyst	T (h)	Ethanol con-version[a] (%)	Isobutanol yield[a] (%)	Isobutanol selectivity[a] (%)	Ref.
trans-[Ru(Cl)$_2$(dppm)$_2$]	2	88.4	64.6	92.8	34a
2	2	51.4	38.1	87.7	16
9	2	40.8	11.1	73.1	

Conditions: catalyst (0.1 mol%), EtOH (1 cm^3), MeOH (10 cm^3, 14.4 equiv.), NaOMe (2 equiv.).[a] Percentages for the liquid phase, analysed by GC.

phosphinophosphinine 1. cis-[Ru(Cl)$_2$(dppm)$_2$] showed no cata-lytic activity at 0.1 mol% loading with KO^{t}Bu (0.5 mol%) in ^{i}PrOH, and heating the reaction mixture to 82 1C for 16 h still did not show any reaction. This was not anticipated because cis/ trans-[Ru(Cl)$_2$(dppm)$_2$] are reported to be highly-active catalysts for the related hydrogen-borrowing reaction where ethanol and methanol is ''upgraded'' to isobutanol,[34] a reaction which com-plex 2 catalyses.[16] The Guerbet-type upgrading of EtOH to n-butanol and EtOH/MeOH to isobutanol is of considerable recent interest[35] because of their use as advanced biofuels.[36] To extend our initial study on the use of phosphinophosphinine 1 in the 'hydrogen-borrowing' production of isobutanol, complex 9 was evaluated to facilitate comparison with trans-[Ru(Cl)$_2$(dppm)$_2$] and 2 (Table 4). In comparison to complex 2, 9 produced a lower conversion (40.8%) of ethanol and gave a lower yield of the desired isobutanol in two hours with moderate selectivity (73.1%). How-ever, GC analysis of the reaction mixture revealed the presence of n-propanol (4.1% yield), which is an intermediate in the formation of isobutanol, indicating that the reaction was not complete.[16,34]
A similar result was observed for 2, with 5.3% n-propanol still left after 2 h.[16]

Conclusions

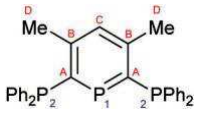
Contrary to the reaction of PhCRCPPh$_2$ with diazaphos-phinine 3, the reaction of MeCRCPPh$_2$ with 3 yielded both the 2,6- and 2,5-bis(diphenylphosphino)phosphinine regioisomers. These isomeric compounds were separated based on their different solubilities and recrystallisation allowed the determination of their molecular structures by X-ray crystallography. Although the reaction of the 2,6-isomer with mesityl azide generated the analogous bis(iminophosphorane) compound 7, its coordina-tion chemistry to late transition metals was not successful, possibly due to the widely contrasting donor-properties of the iminophosphorane and phosphinine donors. Extending the coordination chemistry of the 2-phosphinophosphinine 1 with additional Ru precursors revealed the preferential displace-ment of para-cymene over displacement of the Ru–Cl dative bonds to form an asymmetric dinuclear intermediate. Coordi-nation of 1 to [Ru(Z^6-C$_6$Me$_6$)] and [RuCp*] fragments exposed the coordinated phosphinine to reaction with trace quantities of water, revealing in both cases the syn-addition of H_2O across

a localised PQC double bond. None of the Ru complexes, or cis-[Ru(Cl)$_2$(dppm)$_2$], functioned as precatalysts for the transfer hydrogenation of acetophenone, although the cationic Z^6-C_6Me_6 complex 9 was active in the hydrogen-borrowing upgrading of EtOH/MeOH to isobutanol, with lower yields observed compared to those found previously for 2.

Experimental

All reactions and product isolations were performed under an oxygen-free nitrogen atmosphere using standard Schlenk line techniques or by using an MBRAUN UNIlab Plus glovebox, unless otherwise noted. Anhydrous toluene, dichloromethane, acetonitrile and THF were obtained from an MBRAUN SPS-800 solvent purification system. 40–60 petroleum ether was dis-tilled from sodium wire under nitrogen. Chloroform, $CDCl_3$, hexamethyldisiloxane (HMDSO), pivalonitrile, and triethyla-mine were distilled from calcium hydride. Isopropanol and CD_2Cl_2 were dried over 4 Å molecular sieves. Benzene-d_6 was dried over molten potassium, distilled under a static vacuum and stored in the glovebox. Anhydrous ethanol and methanol were purchased from Sigma-Aldrich. All anhydrous solvents were degassed before use and stored over activated molecular sieves. Non-dry solvents were used as received from Fisher Scientific. $AgBF_4$ and $AgSbF_6$ were purchased from commercial sources and used in the glovebox as anhydrous salts; Na[B{3,5-$(CF_3)_2C_6H_3$}$_4$] was synthesised and thoroughly dried as des-cribed in the literature.[37] NH_4PF_6 was purchased and used in its hydrated state because reactions with dried NH_4PF_6 led to the formation of multiple products. NMR spectra were recorded at 25 1C, unless otherwise stated, on a Bruker AVIII300, AVIII400 and AVI400, spectrometer using the internal protio resonance as
a reference (^{1}H and ^{13}C{^{1}H} NMR spectra). ^{11}B, ^{29}Si, ^{19}F and ^{31}P were referenced to external samples of BF_3 OEt_2, $SiMe_4$, $CFCl_3$ and 85% H_3PO_4 in H_2O respectively as 0 ppm. 4,6-Di(tert-butyl)-1,3,2-diazaphosphinine,[13a] diphenyl(1-prop-1-ynyl)phosphine,[38] mesityl azide,[39] [Ru(Cl)$_2$(dmso)$_4$],[40] [Ru(Cl)$_2$(Cp*)]$_n$,[41] [{Ru(m$_3$-Cl)(Cp*)}$_4$],[42] [{Ru(Cl)(m-Cl)(p-cymene)}$_2$],[43] [{Ru(Cl)(m-Cl)-(C_6Me_6)}$_2$],[44] and cis-[Ru(Cl)$_2$(dppm)$_2$][45] were prepared according to literature procedures. Mass spectrometry analysis was per-formed at the EPSRC UK National Mass Spectrometry Facility at Swansea University using an Atmospheric Solids Analysis Probe. Electron ionisation mass spectrometry (EI-MS) was carried out using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh. FTIR was performed on a Thermo Scientific Nicolet iS5/iD5 ATR spectrometer. GC-FID analysis of EtOH/MeOH upgrading catalytic samples was carried out on an Agilent 7820A GC
fitted with DB-WAX column 30 m 320 mm, I.D. 0.25 mm. Method: oven temperature starts at 35 1C for 5 minutes, heat to
250 1C at 50 1C min ^{1} then hold at 250 1C for 5 minutes. Flow rate 6.5 cm^3 min ^{1}. Elemental analyses were conducted by Dr Brian Hutton using an Exeter CE-440 elemental analyser at Heriot-Watt University or by Mr Stephen Boyer at London Metropolitan University.

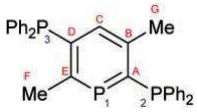
2,6-bis(diphenylphosphino)-3,5-dimethylphosphinine, 5



To a solution of diazaphosphinine (374 mg, 1.78 mmol) in 20 cm^3 toluene was added a solution of diphenyl(prop-1-ynyl)-phosphine (798 mg, 3.56 mmol, 2 equiv.) in toluene (5 cm^3). The solution was heated at 120 1C in an ampoule sealed with a Young's tap until ^{31}P{^{1}H} NMR spectroscopy showed complete conversion of the diazaphosphinine to two isomeric products in a 60 : 40 ratio (ca. 14 d). All volatiles were removed under reduced pressure and the resulting oil was extracted with 40–60 pet. ether (ca. 150 cm^3) and filtered through a glass frit under air before concentration on a rotary evaporator. This extraction was repeated until a signal at d = 244.8 ppm was not observed by ^{31}P{^{1}H} NMR spectroscopy in the solid material. All solvent was removed under reduced pressure and the resulting dark oil was dissolved in the minimum volume of CH_2Cl_2 (ca. 5 cm^3). Pentane (10 cm^3) was layered on top of the solution causing the slow precipitation of a brown crystalline solid. If precipita-tion did not occur, more pentane (50 cm^3) was added and the mixture agitated. The resulting brown precipitate was isolated by filtration and washed with pentane (3 10 cm^3), then dried under vacuum. Recrystallisation from a minimum volume of toluene at 25 1C gave the pure product as a colourless solid (450 mg, 0.91 mmol, 51%). Once isolated, the product is air-stable in the solid state. Crystals suitable for X-ray diffraction were grown from a 10 : 1 solution of anhydrous THF and 40–60 petroleum ether at 25 1C.

^{1}H NMR (400 MHz, $CDCl_3$): d = 7.32–7.20 (m, 20H, 2 PPh_2), 7.18–7.14 (m, 1H, H_C), 2.48 (s, 6H, H_D); ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): d = 244.8 (t, P_1, $^2J_{P–P}$ = 38.9 Hz), 8.1 (d, 2P, P_2, $^2J_{P–P}$ = 38.9 Hz); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): d = 164.22 (dd, 2C, C_A, $^1J_{CA–P1}$ = 84.5 Hz, $^1J_{CA–P2}$ = 24.1 Hz), 147.38 (dd, 2C, C_B, $^2J_{CB–P1}$ = 23.1 Hz, $^2J_{CB–P2}$ = 11.1 Hz), 136.1 (t, C_C, $^3J_{CC–P2}$ = 9.8 Hz) 134.1 (m, 2 PPh_2), 128.7 (s, 2 PPh_2), 128.3 (d, 2 PPh_2), 23.5 (d, 2C, C_D, $^3J_{CD-P}$ = 23.1 Hz); EI: m/z: 492.1 ([M]$^+$); elemental analysis: Anal. calcd for $C_{31}H_{27}P_3$: C 75.61, H 5.53. Found: C 75.50, H 5.49.

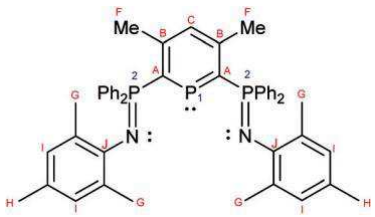
2,5-Bis(diphenylphosphino)-3,6-dimethylphosphinine, 6



The pet. ether insoluble solid from the previous procedure was mixed with sand and transferred to a Soxhlet thimble. This was then extracted with boiling n-hexane (300 cm^3) using a Soxhlet apparatus for one week under air. Over the course of the extraction, a white precipitate formed that was isolated by filtration and washed with hexane (3 10 cm^3), then dried under reduced pressure. The product was then recrystallized from a minimum volume of toluene at 25 1C, yielding the pure product as a colourless solid (190 mg, 0.39 mmol, 22%). Single crystals suitable for X-ray diffraction were grown by slow diffusion of ether into a THF solution.

^{1}H-NMR (300 MHz, $CDCl_3$): d = 7.45–7.31 (m, 20H, 2 PPh_2) 6.74 (bs, 1H, H_C), 2.61 (d, 3H, H_F, $^3J_{HF–P1}$ = 16.0 Hz), 2.29 (s, 3H, H_G); $^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$): d = 220.3 (dd, P_1, $^2J_{P1–P2}$ = 29.2 Hz, $^3J_{P1–P3}$ = 4.9 Hz), 9.2 (dd, P_2, $^2J_{P2–P1}$ = 29.2 Hz, $^5J_{P2–P3}$ = 2.3 Hz), 10.8 (dd, P_3, $^3J_{P3–P1}$ = 4.9 Hz, $^5J_{P3–P2}$ = 2.3 Hz); $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): d = 169.6 (dd, C_E, $^1J_{CE–P1}$ = 59.9 Hz, $^2J_{CE–P3}$ = 19.2 Hz), 167.1 (dd, C_A, $^1J_{CA–P1}$ = 75.1 Hz, $^2J_{CA–P2}$ = 24.0 Hz), 145.3 (dd, C_B, $^2J_{CB–P1}$ = 22.4 Hz, $^2J_{CB–P2}$ = 12.8 Hz), 142.6 (dd, C_D, $^1J_{CD–P1}$ = 22.4 Hz, $^2J_{CD–P3}$ = 12.8 Hz), 136.5 (m, C_C, $^3J_{CC–P1}$ = 15.2 Hz), 136.0 (t, PPh_2, J = 8.8 Hz), 135.7 (d, PPh_2, J = 11.2 Hz), 134.3(t, PPh_2, J = 20.0 Hz), 129.1–128.5 (m, PPh_2), 23.8 (d, C_G, $^3J_{CG-P1}$ = 24.1 Hz), 23.5 (dd, C_F, $^2J_{CF–P1}$ = 43.3 Hz, $^3J_{CF–P3}$ = 24.1 Hz); EI: m/z: 492.1 ($[M]^+$); Elemental analysis: Anal. calcd for $C_{31}H_{27}P_3$: C 75.61, H 5.53. Found: C 75.47, H 5.71.

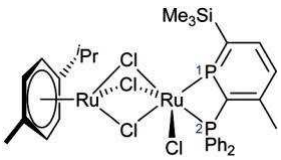
2,6-Bis{diphenyl(N-mesityl)iminophosphorano}-3,5-dimethylphosphinine, 7



To a Schlenk flask containing freshly recrystallized 2,6-bis(diphenylphosphino)-3,5-dimethylphosphinine, 5 (432 mg, 0.88 mmol, 1 equiv.) was added sequentially anhydrous HMDSO (15 cm^3) and mesityl azide (311 mg, 1.93 mmol, 2.2 equiv.). The heterogeneous mixture was heated under reflux for 24 h, forming a bright yellow precipitate. Once cool, the precipitate was isolated by cannula filtration and washed with anhydrous HMDSO (10 cm^3). The product was dried overnight under high vacuum, yielding a yellow solid (564 mg, 0.74 mmol, 85%). An analytically pure sample was obtained by recrystallization from toluene at 25 1C.

^{1}H-NMR (400 MHz, $CDCl_3$): d = 7.75–7.70 (m, 8H, 2 o-PPh_2) 7.05–6.83 (m, 16H, 2 m,p-PPh_2, H_I), 6.71 (s, 1H, H_C), 2.49 (s, 6H, H_F), 2.32 (s, 6H, H_H), 2.24 (s, 12H, H_G); $^{31}P\{^1H\}$-NMR (162 MHz, $CDCl_3$): d = 246.9 (t, P_1, $^2J_{P1–P2}$ = 99.7 Hz), 9.4 (d, 2P, P_2, $^2J_{P2–P1}$ = 99.7 Hz); $^{13}C\{^1H\}$-NMR (100 MHz, $CDCl_3$): d = 160.0–158.4 (m, 2C, C_A), 151.5–151.2 (m, 2C, C_B), 145.1 (s, 2C, C_J), 139.3–138.9 (m, C_C), 134.0–129.0 (m, C_I & 2 PPh_2), 24.3 (m, 2C, C_F), 21.1 (s, 4C, C_G), 20.6 (s, 2C, C_H); HRMS (ASAP/QTof): m/z: ($[M + H]^+$) calcd for $C_{49}H_{50}N_2P_3$: 759.3187; found: 759.3196; Elemental analysis: Anal. calcd for $C_{49}H_{49}N_2P_3$: C 77.56, H 6.51, N 3.69. Found: C 77.55, H 6.42, 3.68.

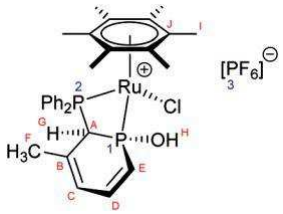
Compound 8



An NMR tube equipped with a J. Young tap was charged with 2-diphenylphosphino-3-methyl-6-trimethylsilylphosphinine, 1 (20 mg, 0.05 mmol, 1 equiv.), [{Ru(Cl)(m-Cl)(p-cymene)}$_2$] (17 mg, 0.03 mmol, 0.5 equiv.) and C_6D_6 (0.6 cm^3) then sealed under N_2. The reaction was heated to 50 1C for 5 min then layered with 40–60 pet. ether (1.2 cm^3). Dark red crystals of 8 were then manually separated from the yellow crystals of 2 for X-ray analysis.

$^{31}P\{^1H\}$-NMR (162 MHz, CDCl3): d = 231.4 (d, P_1, $^2J_{P1–P2}$ = 55.5 Hz), 21.7 (d, P_2, $^2J_{P2–P1}$ = 55.5 Hz).

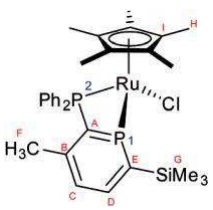
Chloro(hexamethylbenzene)(1-hydroxy-2-diphenylphosphino-3-methylphosphacyclohexa-3,5-diene)ruthenium(II) hexafluorophosphate, 9



To a Schlenk flask containing 2-diphenylphosphino-3-methyl-6-trimethylsilylphosphinine, 1 (71 mg, 0.19 mmol, 1 equiv.), [{Ru(Cl)(m-Cl)(C_6Me_6)}$_2$] (65 mg, 0.1 mmol, 0.5 equiv.) and NH_4PF_6 (32 mg, 0.19 mmol, 1 equiv.) was added anhydrous CH_2Cl_2 (15 cm^3) and the resulting heterogeneous mixture was vigorously stirred for 64 h. The solution was filtered to remove NH_4Cl and then concentrated to ca. 1 cm^3 under reduced pressure before being layered with 40–60 pet. ether (10 cm^3). Once crystallisation was complete, the supernatant solvent was removed by cannula filtration and the orange needles of product (113 mg, 0.15 mmol, 78%) manually separated from a white solid.

^{1}H-NMR (400 MHz, CD_2Cl_2): d = 7.79–7.60 (m, 7H, PPh_2 & H_E), 7.54–7.50 (m, 2H, PPh_2), 7.24–7.19 (m, 2H, PPh_2), 6.96 (ddd, 1H, H_D, $^3J_{HD–P1}$ = 33.75 Hz, $^3J_{HD–HE}$ = 12.32 Hz, $^3J_{HD–HC}$ = 7.04 Hz), 6.59 (dd, 1H, H_H, $^2J_{HH–P1}$ = 24.06 Hz, $^2J_{HH–HE}$ = 12.32 Hz), 5.89 (bs, 1H, H_C), 5.32 (t, 1H, H_G, $^2J_{HG–P1}$ = 15.55 Hz), 2.20 (s, 18H, H_I), 1.65 (s, 3H, H_F); $^{31}P\{^1H\}$-NMR (162 MHz, CD_2Cl_2): d = 11.6 (d, P_1, $^2J_{P1–P2}$ = 97.1 Hz), 8.8 (d, P_2, $^2J_{P2–P1}$ = 97.1 Hz), 144.5 (sept, P_3, $^1J_{P3-F}$ = 711.4 Hz); $^{19}F\{^1H\}$-NMR (79 MHz, CD_2Cl_2): d = 73.3 (d, 6F, PF_6, $^2J_{F–P3}$ = 709.5 Hz); HRMS (ASAP/QTof): m/z: ($[M\ PF_6]^+$) calcd for $C_{30}H_{36}ClOP_2Ru$: 611.0978; found: 611.0983; Elemental analysis: Anal. calcd. for $C_{30}H_{36}ClF_6OP_3Ru$: C 47.66, H 4.80; found: C 47.89, H 5.17.

Chloro(pentamethylcyclopentadienyl)(2-diphenylphosphino-3-methyl-6-trimethylsilylphosphinine)ruthenium(II), 10

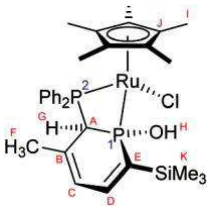


To a Schlenk flask containing 2-diphenylphosphino-3-methyl-6-trimethylsilylphosphinine, 1 (30 mg, 0.08 mmol, 1 equiv.) and

[{Ru(μ3-Cl)(Cp*)}4] (22 mg, 0.02 mmol, 0.25 equiv.) was added anhydrous THF (2 cm3). The resulting deep red solution was stirred for 5 minutes before the solvent was removed under reduced pressure. The resulting oily solid was then dissolved in 40–60 pet. ether (5 cm3) and the solution cooled to 0 1C until an orange precipitate was observed. The precipitate was isolated by cannula filtration and dried under high vacuum yielding a highly air-sensitive orange powder, (36 mg, 0.06 mmol, 70%).

^{1}H-NMR (400 MHz, C_6D_6): d = 8.24–8.19 (m, 2H, PPh_2), 7.63 (dd, 1H, H_D, $^3J_{HD–P1}$ = 22.51 Hz, $^3J_{HD–HC}$ = 8.48 Hz), 7.41–7.36 (m, 2H, PPh_2), 7.22–6.93 (m, 6H, PPh_2), 6.46 (app. dt, 1H, H_C, $^3J_{HC–HD}$ = 8.48 Hz, $^4J_{HC–P1}$ = 2.92 Hz, $^4J_{HC–P2}$ = 2.63 Hz), 1.74 (s, 3H, H_F), 1.62 (t, 15H, H_H, $^3J_{HH–P1}$ = 2.05 Hz), 0.47 (s, 9H, H_F); ^{31}P{^{1}H}-NMR (162 MHz, C_6D_6): d = 240.1 (d, P_1, $^2J_{P1–P2}$ = 6.9 Hz), 18.2 (d, P_2, $^2J_{P2–P1}$ = 6.9 Hz); ^{13}C{^{1}H}-NMR (126 MHz, $CDCl_3$): d = 168.8 (d, C_E, $^1J_{CE–P1}$ = 18.0 Hz), 151.3 (dd, C_A, $^1J_{CA–P1}$ = 61.4 Hz, $^1J_{CA–P2}$ = 19.1 Hz), 146.6 (dd, C_B, $^2J_{CB–P1}$ = 11.1 Hz, $^2J_{CB–P2}$ = 7.9 Hz), 144.1 (dd, C_D, $^2J_{CD–P1}$ = 17.1 Hz, $^4J_{CD–P2}$ = 3.4 Hz), 135.5 (d, PPh_2, J = 12.0 Hz), 134.2 (dd, PPh_2, J = 37.9, 6.5 Hz), 132.0 (d, PPh_2, J = 9.9 Hz), 130.3 (dd, PPh_2, J = 23.4 Hz, 14.6 Hz), 129.9 (d, PPh_2, J = 2.4 Hz), 129.1 (d, PPh_2, J = 2.1 Hz), 123.6 (dd, C_C, $^3J_{CC–P1}$ = 32.7 Hz, $^3J_{CC–P2}$ = 6.1 Hz), 89.1 (ap. t, 5C, C_I, $^2J_{CI–P1}$ = 2.6 Hz, $^2J_{CI–P2}$ = 2.5 Hz), 21.6 (ap. t, C_F, $^3J_{CF–P1}$ = 6.7 Hz, $^3J_{CF–P2}$ = 6.7 Hz) 10.4 (s, 5C, C_H), 0.0 (d, 3C, C_G, $^3J_{CG–P1}$ = 3.5 Hz); ^{29}Si{^{1}H}-NMR (79 MHz, $CDCl_3$): d = 2.4 (dd, $SiMe_3$, $^2J_{Si–P1}$ = 22.0 Hz, $^4J_{Si–P2}$ = 3.0 Hz); HRMS (ASAP/QTof): m/z: ([M Cl]$^+$) calcd for $C_{31}H_{39}P_2RuSi$: 603.1348; found: 603.1347.

Chloro(pentamethylcyclopentadienyl)(1-hydroxy-2-diphenylphosphino-3-methyl-6-trimethylsilylphospha-cyclohexa-3,5-diene) ruthenium(II), 11



2-Diphenylphosphino-3-methyl-6-trimethylsilylphosphinine (76 mg, 0.2 mmol, 1 equiv.) and [{Ru(μ3-Cl)(Cp*)}4] (56 mg, 0.05 mmol, 0.25 equiv.) were dissolved in THF (5 cm3). After removal of the solvent, the residue was dissolved in 40–60 pet. ether (5 cm3) and stored at 5 1C in the presence of atmospheric moisture for 30 days. Small red crystals formed, which were isolated by

Table 5 Crystallographic data for compounds 5, 6, 7Fe, 8, 9 and 11

Compound	5	6	7Fe 4(CH_2Cl_2)	8	9 0.5(CH_2Cl_2)	11
Empirical formula	$C_{31}H_{27}P_3$	$C_{31}H_{27}P_3$	$C_{53}H_{60}Cl_{11}FeN_2OP_3$	$C_{31}H_{38}Cl_4P_2Ru_2Si$	$C_{30.5}H_{37}Cl_2F_6OP_3Ru$	$C_{31}H_{41}ClOP_2RuSi$
Formula weight	492.43	492.43	1279.74	844.58	798.48	656.19
Temperature/K	100	100	100	100	150	120
Crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	Monoclinic	Triclinic
Space group	% P1	$P2_1/n$	% P1	% P1	$P2_1/n$	% P1
a/Å	7.5692(9)	9.9671(13)	12.3741(5)	9.8194(5)	8.8172(4)	14.6758(5)
b/Å	12.6145(16)	8.0650(11)	14.0430(5)	10.9184(6)	37.4359(16)	14.7658(4)
c/Å	15.2354(17)	15.9450(18)	19.6151(7)	16.7816(9)	19.6657(9)	15.2176(3)
a/1	69.228(5)	90	104.833(2)	99.502(3)	90	92.281(2)
b/1	76.539(5)	99.576(9)	93.541(2)	94.824(3)	90.340(2)	105.461(2)
g/1	73.790(5)	90	114.316(2)	105.119(3)	90	101.298(2)
Volume/Å^3	1291.5(3)	1263.9(3)	2948.1(2)	1697.74(16)	6491.1(5)	3101.93(15)
Z	2	2	2	2	8	4
r_{calc} g cm^{-3}	1.266	1.294	1.442	1.652	1.634	1.405
m/mm^{-1}	0.248	0.254	0.875	1.355	0.855	6.394
F(000)	516	516	1316	848	3240	1360
Crystal size/mm^3	0.40 0.40 0.15	0.17 0.10 0.10	0.38 0.22 0.10	0.20 0.20 0.20	0.27 0.27 0.19	0.20 0.05 0.02
Radiation	MoKa (l = 0.71073)	MoKa (l = 0.71073)	MoKa (l = 0.71073)	MoKa (l = 0.71073)	MoKa (l = 0.71073)	CuKa (l = 1.54184)
2Y range for data collection/1	3.536 to 60.984	5.24 to 55.118	3.678 to 55.62	5.276 to 55.356	4.68 to 56.784	7.478 to 152.286
Index ranges	10 r h r 10, 17 r k r 17, 21 r l r 20	12 r h r 11, 10 r k r 8, 20 r l r 20	16 r h r 15, 18 r k r 18, 25 r l r 25	12 r h r 12, 14 r k r 14, 21 r l r 21	11 r h r 11, 50 r k r 49, 26 r l r 26	18 r h r 17, 18 r k r 17, 18 r l r 19
Reflections collected	34 832	9164	51 076	50 022	222 582	49 418
Independent reflections	7806 [R_{int} = 0.0276, R_{sigma} = 0.0291]	2854 [R_{int} = 0.0756, R_{sigma} = 0.1155]	13 575 [R_{int} = 0.0345, R_{sigma} = 0.0395]	7730 [R_{int} = 0.0489, R_{sigma} = 0.0403]	16 043 [R_{int} = 0.0388, R_{sigma} = 0.0188]	12 852 [R_{int} = 0.0820, R_{sigma} = 0.0664]
Data/restraints/ parameters	7806/0/309	2854/54/192	13 575/2/657	7730/0/368	16 043/2/810	12 852/1/697
Goodness-of-fit on F^2	1.044	1.051	1.158	1.062	1.127	1.045
Final R indexes [I r 2s(I)]	R_1 = 0.0331, wR_2 = 0.0823	R_1 = 0.0779, wR_2 = 0.1361	R_1 = 0.0525, wR_2 = 0.1045	R_1 = 0.0308, wR_2 = 0.0618	R_1 = 0.0422, wR_2 = 0.0973	R_1 = 0.0516, wR_2 = 0.1277
Final R indexes [all data]	R_1 = 0.0424, wR_2 = 0.0873	R_1 = 0.1452, wR_2 = 0.1601	R_1 = 0.0605, wR_2 = 0.1081	R_1 = 0.0445, wR_2 = 0.0659	R_1 = 0.0493, wR_2 = 0.1009	R_1 = 0.0635, wR_2 = 0.1358
Largest diff. peak/hole/e Å^{-3}	0.37/ 0.24	0.81/ 0.53	0.62/ 0.84	0.56/ 0.76	1.25/ 0.94	1.04/ 1.39

cannula filtration and dried under high vacuum yielding a red crystalline powder (16 mg, 0.02 mmol, 12%).

^{1}H-NMR (400 MHz, CD_2Cl_2): d = 7.76–7.14 (m, 10H, PPh_2), 6.67 (dd, 1H, H_D, $^3J_{HD–P1}$ = 36.68 Hz, $^3J_{HD–HC}$ = 6.75 Hz), 6.48 (bs, 1H, H_H), 5.81 (d, 1H, H_C, $^3J_{HC–HD}$ = 6.46 Hz), 5.08 (app. t, 1H, H_G, $^2J_{HG–P1}$ = 12.32 Hz, $^2J_{HG–P2}$ = 12.03 Hz), 1.59 (t, 15H, H_I, $^3J_{HI–P1}$ = 2.05 Hz), 1.39 (s, 3H, H_F), 0.37 (s, 9H, H_K); ^{31}P{^{1}H}-NMR (162 MHz, CD_2Cl_2): d = 78.3 (d, P_1, $^2J_{P1–P2}$ = 59.5 Hz), 18.0 (d, P_2, $^2J_{P2–P1}$ = 59.5 Hz);^{29}Si{^{1}H}-NMR (79 MHz, CD_2Cl_2): d = 2.7 (d, $SiMe_3$, $^2J_{Si–P1}$ = 15.6 Hz); HRMS (ASAP/QTof): m/z: ([M Cl H_2O]$^+$) calcd for $C_{31}H_{39}P_2RuSi$: 603.1348; found: 603.1360; Elemental analysis: Anal. calcd for $C_{31}H_{41}ClOP_2RuSi$: C 56.73, H 6.30; found: C 56.73, H 6.52.

Procedure for transfer hydrogenation catalysis

To a dry Schlenk flask, under N_2 and equipped with a stirrer bar, was added a known amount of 1,3,5-trimethoxybenzene, ^{i}PrOH, the substrate (1 mmol) and a stock solution of 2 (0.1 mol%) and KO^{t}Bu (0.5 mol%) in ^{i}PrOH, to a total solvent volume of 2.3 cm^3. After 1 hour, 0.1 cm^3 was removed by syringe and its ^{1}H-NMR spectrum ($CDCl_3$) recorded, the reaction was then quenched by admission of air into the flask. Reactions at 82 1C were run in a 50 cm^3 ampoule fitted with a Teflon tap.

Procedure for the catalytic upgrading of ethanol and methanol to isobutanol

2 (0.015 g, 0.017 mmol, 0.1 mol%), and NaOMe (1.85 g, 34.26 mmol, 200 mol%) were added to a clean oven-dried fitted PTFE insert inside a glove box. The insert was sealed within a 100 cm^3 Parr stainless steel autoclave which was then transferred to a N_2/vacuum manifold. Methanol (10 cm^3) was injected into the autoclave through an inlet against a flow of nitrogen followed by ethanol (1 cm^3, 17.13 mmol). The autoclave was sealed and placed into a pre-heated (180 1C) aluminium heating mantle. After the reaction run time (2 h), the autoclave was cooled to room temperature in an ice-water bath. The autoclave was vented to remove any gas generated during the reaction. A liquid sample was removed, filtered through a short plug of alumina (acidic) and analysed by GC (100 mL of sample, 25 mL of hexadecane standard, 1.7 cm^3 Et_2O – sample filtered through a glass filter paper to remove insoluble salts).

Crystallographic details

Single crystals of the samples were covered in an inert oil and placed under the cold stream of the diffractometer. Exposures were collected and indexing, data collection and absorption correction were performed using either the APEXII suite of programs on a Bruker X8 APEXII four-circle diffractometer or with CrysalisPro interfacing an Oxford Diffraction four-circle Supernova diffractometer (University of Edinburgh). Structures were solved using direct methods (SHELXT) and refined by full-matrix least-squares (SHELXL)[46] interfaced with the pro-gramme OLEX2[47] (Tables 5). 2,5-Bis(diphenylphosphino)-3,6-dimethylphosphinine (6) showed the central phosphinine ring and Me substituents to be disordered, and this was successfully modelled equally over two positions.

Conflicts of interest

There are no conflicts to declare.

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